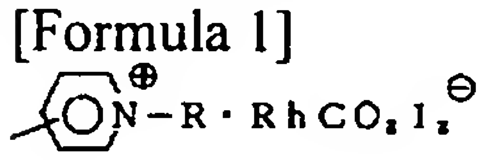

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of the acetic acid which uses as a reaction raw material the oxygenated compound chosen from a methanol and wood ether, and a carbon monoxide.
[0002]
[Description of the Prior Art] In order to manufacture an acetic acid, the method of carrying out the carbonylation reaction of a methanol and the carbon monoxide under existence of iodation.alkyl and in an organic solvent is learned, using the rhodium complex which the vinylpyridine system resin which has the porosity structure of cross linkage was made to support as a catalyst for a carbonylation reaction (JP,6-315637,A). In the carbonylation reaction process of this methanol, reaction generation liquid and reaction generation gas are obtained. The organic solvent and iodation alkyl which used reaction generation liquid on the occasion of by-product; reactions, such as unreacted methanol:methyl acetate besides the acetic acid generated by the carbonylation reaction of a methanol, a propionic acid, water, and hydrogen iodide; the rhodium complex desorbed from vinylpyridine system resin is contained. The by-product of CO2 and H2 besides a carbon monoxide with reaction generation gas unreacted on the other hand, and CH4 grade; the iodation alkyl used on the occasion of the reaction is contained. By the way, in order that reaction generation liquid may carry out separation recovery of the acetic acid contained in it, distillation processing is carried out, but if distillation processing of the reaction generation liquid is carried out as it is in this case, in the rhodium complex contained in reaction generation liquid, it will shift into a distillate or distillation residue liquid, and un-arranging, such as becoming with the purity fall cause of an acetic acid, will be generated. Moreover, in a distillation process, for the reasons of a deposit etc., it does not circulate through some rhodium complexes at a reaction process, but they are lost with distillation residue liquid. Since the rhodium complex is expensive, such loss is not desirable from the point of the economical efficiency of a process. Therefore, although it is desirable to carry out separation recovery from reaction generation liquid, and to circulate at a reaction process before the rhodium complex contained in reaction generation liquid distills reaction generation liquid, the method of now separating the rhodium complex contained in it from reaction generation liquid efficiently and economically is not yet developed.
[0003]
[Problem(s) to be Solved by the Invention] This invention makes it the technical problem to offer the manufacture approach of an acetic acid including the process which separates the rhodium complex contained in it from reaction generation liquid efficiently and economically.
[0004]
[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. Namely, according to this invention, the oxygenated compound chosen from a methanol and wood ether and a carbon monoxide are set to the manufacture approach of the acetic acid used as a reaction raw material. (i) The

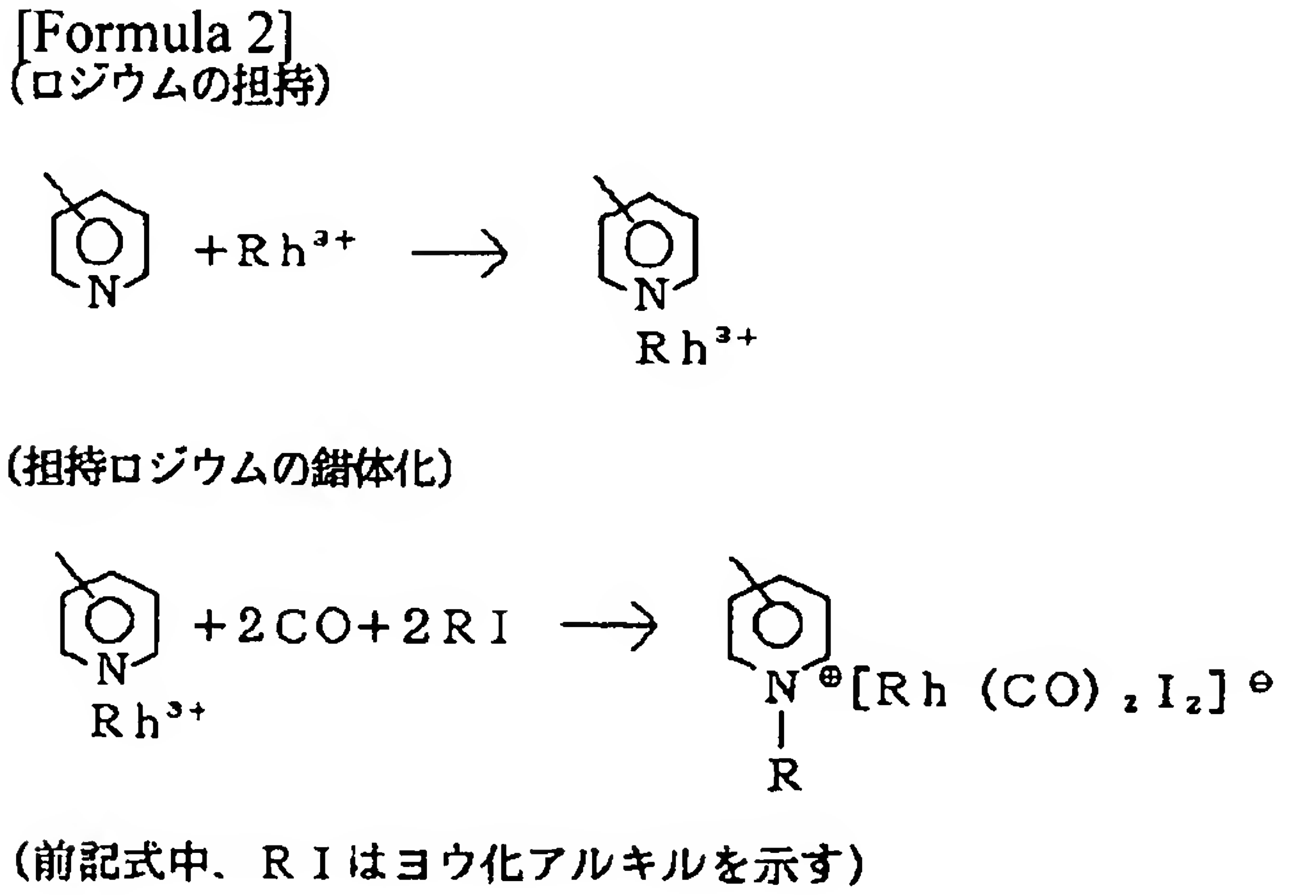
solid-state catalyst containing a rhodium complex is used. Under existence of iodation alkyl, The carbonylation reaction process of making an oxygenated compound and a carbon monoxide reacting in an organic solvent, and making an acetic acid generating, (ii) The reaction generation liquid obtained at this carbonylation reaction process is contacted to the adsorbent in which adsorbent is shown to a rhodium complex. The reaction generation gas obtained at the adsorption process to which the rhodium complex contained in reaction generation liquid is made to stick, and this (iii) carbonylation process is contacted to an oxygenated compound and/or an organic solvent. The iodation alkyl recovery process of dissolving the iodation alkyl contained in reaction generation gas in an oxygenated compound and/or an organic solvent, (iv) The heavy component which distills reaction generation liquid after the rhodium complex obtained by this adsorption process was separated, and consists of an acetic acid, The distillation process divided into the more volatile component which consists of iodation alkyl, methyl acetate, and water, (v) the oxygenated compound and/or organic solvent containing the iodation alkyl obtained at this iodation alkyl recovery process The desorption process to which desorption of the rhodium complex which is contacted to the adsorbent which adsorbed the rhodium complex, and by which the adsorbent is adsorbed is carried out, (vi) -- the circulation process which circulates the liquid containing the rhodium complex which may be this desorption process to said carbonylation reaction process -- since -- the manufacture approach of the acetic acid characterized by becoming is offered.
[0005]
[Embodiment of the Invention] The support used for rhodium complex support by this invention is vinylpyridine system resin (henceforth VP resin) which has the porosity structure of cross linkage. In the case of VP resin used by this invention, the degree of cross linking is usually specified to 30 - 60% 10 to 70%. When using a catalyst at an elevated temperature, for example, 50-180 degrees C, it is good to specify preferably the degree of cross linking of the VP resin to 50 - 60% 30% or more. If the degree of cross linking of VP resin becomes lower than said range, since the thermal resistance of VP resin and a mechanical strength will become low and the endurance of a catalyst and abrasion resistance will fall, it is not desirable. On the other hand, if the degree of cross linking exceeds said range, since the activity of a catalyst will become inadequate, it is not desirable.
[0006] although said VP resin used by this invention is what has a vesicular structure -- the surface area -- 5-80m2/g -- it is 10-40m2/g preferably, and the pore volume is 0.2 - 0.4 cc/g preferably 0.15 to 0.5 cc/g, and 20-100nm of the average pole diameter is 30-90nm preferably. If the pore volume of VP resin becomes smaller than said range, since the problem of a fall of catalytic activity will be produced, if it becomes larger than said range desirable on the other hand, since problems, such as a wear-resistant fall of VP resin, will be produced, it is not desirable. Furthermore, if the average pole diameter of VP resin becomes smaller than said range, since the problem of a fall of catalytic activity will be produced, if it becomes larger than said range desirable on the other hand, since problems, such as a wear-resistant fall of VP resin, will be produced, it is not desirable.
[0007] In this specification, the degree of cross linking said about VP resin is defined as follows. Moreover, the pore volume and surface area which are said about VP resin are the following, and are made and measured. Furthermore, the average pole diameter said about VP resin is the following, and is made and computed.
(Degree of cross linking)
Weight B of the cross linking agent contained in degree-of-cross-linking (%) =A/Bx100A:resin: It measured by the approach (the so-called method of mercury penetration) using the weight (pore volume) Mercury pressure polo C meter model 70 (made in [of Italy country Milan] Carlo Elba) of the vinylpyridine system monomer contained in resin. In this case, surface tension of mercury was made into 474 dyne/cm at 25 degrees C, and the use contact angle was made into 140 degrees, absolutely, it changed the mercury pressure force to 1-200kg/cm2, and measured it.
(Surface area) It was measured by B.E.T law.
(Average pole diameter) It computed by the following formulas using each measured value of the pore volume which is the above, and was made and measured, and surface area.
Average pole-diameter (nm) =4(C/D) x103C: Pore volume (cc/g)

D: Surface area (m2/g)
[0008] VP resin is manufactured by carrying out copolymerization of the compound with two vinyl groups as a cross linking agent to a vinylpyridine system monomer. 4-vinylpyridine, 2-vinylpyridine, etc. are mentioned as a vinylpyridine system monomer used in order to obtain VP resin. Moreover, aliphatic series system vinyl monomers, such as aromatic series system vinyl monomers, such as other vinyl monomers, for example, styrene, and vinyltoluene, or a methyl acrylate, and a methyl methacrylate, are mixable into this vinylpyridine system monomer. The amount of mixing of these vinyl monomers is good less than [30 mol %] and to make [all the inside of a monomer, and] it preferably less than [20 mol %]. The cross linking agent which carries out copolymerization to said vinylpyridine system monomer is a compound which has two vinyl groups. As such a thing, aliphatic compounds, such as diacrylic acid ethylene glycol besides aromatic compounds, such as a divinylbenzene and divinyl toluene, and a butadiene, can be mentioned. Although the divinylbenzene used industrially usually contains about 50-mol % ethyl vinylbenzene, such a divinylbenzene can also be used in this invention. The amount of this cross linking agent used is suitably decided according to the degree of cross linking of VP resin for which it asks. Said VP resin is explained by JP,6-315637,A in full detail.
[0009] The particle size of VP resin is more preferably used as a 0.4-2mm granule 0.1-2mm 0.01-4mm, and the desirable configuration is a spherule.
[0010] The catalyst used by this invention consists of a rhodium complex which VP resin was made to support. The amount of support of a rhodium complex is the amount of metal rhodium conversions to VP resin, and is 0.5 - 1% of the weight of the range preferably 0.2 to 2% of the weight.
[0011] One example of the desirable catalyst used by this invention is formed in the pyridine ring which the rhodium complex anion by which a part of pyridine ring [at least] contained in VP resin is expressed with the following type (1) combined.
[Formula 1]



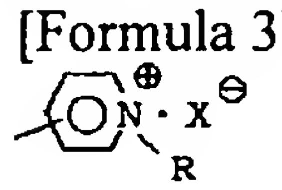
(1)

R shows hydrogen or a low-grade alkyl group among said formula.
[0012] VP resin which has the pyridine ring which the rhodium complex anion used as a catalyst by this invention combined can be obtained by the following approaches.
(1) How to make it change to a rhodium complex under existence of iodation alkyl and a carbon monoxide in an organic solvent after making the nitrogen atom of the pyridine ring of VP resin support rhodium ion in a water solution.
The reaction of the pyridine ring and rhodium in this approach is expressed with a degree type. Moreover, generally as the reaction condition, support of a rhodium can use the conditions as the carbonylation conditions of a methanol that complex-izing of a support rhodium is the same for the conditions under ordinary temperature and ordinary pressure.
[0013]
[Formula 2]



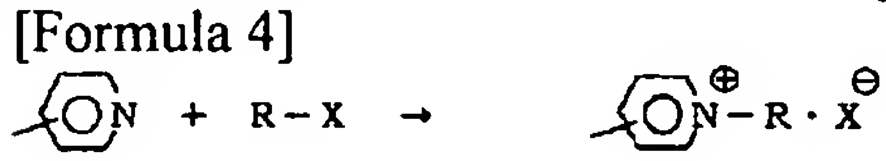
(2)

[0014] (2) How to contact VP resin in a rhodium salt in the solvent which contains iodation alkyl under carbon monoxide pressurization.
What is necessary is just to contact a rhodium salt and VP resin under the carbonylation reaction condition of a methanol generally in the case of this approach. In the catalytic reaction in this case, the pyridine ring contained in VP resin is formed into 4 class by iodation alkyl, it becomes pyridinium salt, and rhodium carbonyl complex [Rh(CO)2I2] ~ generated by the reaction of a rhodium salt, iodation alkyl, and a carbon monoxide to this pyridinium salt joins together in ion.
[0015] as said rhodium salt -- a rhodium chloride and bromination -- carboxylic-acid rhodium salts [, such as a halogenation rhodium; acetic-acid rhodium and a propionic-acid rhodium,], such as a rhodium and an iodation rhodium, are mentioned. Moreover, although what has the low-grade alkyl group of the carbon numbers 1-5, such as a methyl iodide, an ethyl iodide, and propyl iodide, is mentioned as iodation alkyl, especially use of a methyl iodide is desirable. The operating rate of iodation alkyl to a rhodium salt is 50-500 mols in rate preferably per one mol of rhodium salts, and 2-2000 mols of iodation alkyls. moreover, the carbon monooxide pressure at the time of contacting a rhodium salt and iodation alkyl -- 7-30kg/cm2G -- it is 10-20kg/cm2G preferably.
[0016] The thing of arbitration is usable if adsorbent is shown to a rhodium complex as an adsorbent used in order to carry out adsorption separation of the rhodium complex contained in reaction generation liquid by this invention. As such an adsorbent, it consists of VP resin and some nitrogen atoms [at least] of the pyridine ring contained in the resin can use what is formed into 4 class, for example. In this VP resin, the pyridine ring which has the 4th class-ized nitrogen atom of that is expressed with the following general formula (3).
[Formula 3]



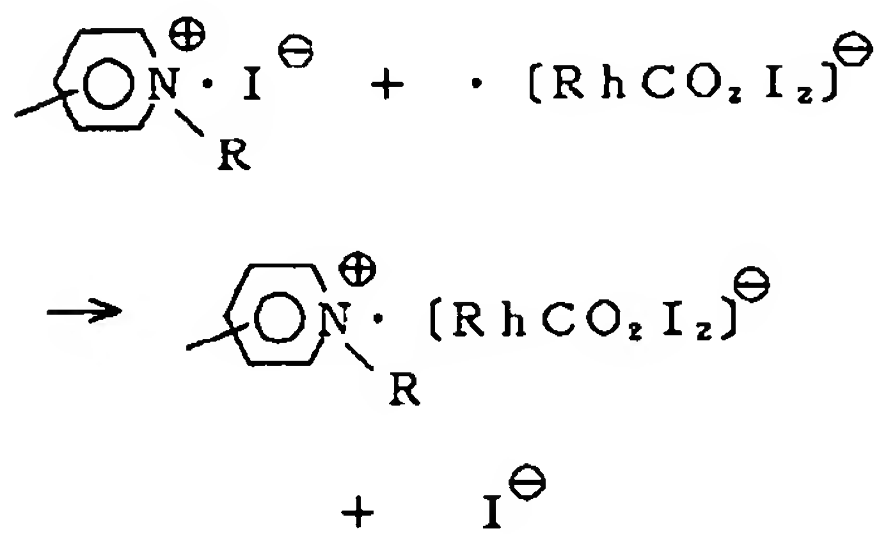
(3)

R shows hydrogen or a low-grade alkyl group among said formula, and X shows a halogen. Desirable R is a methyl group and desirable X is iodine. As said VP resin, VP resin shown above as support for support of a rhodium complex can be used. Although it is desirable to change the all into the pyridine ring of the 4th class-ized structure expressed with said general formula (3) as for the pyridine ring contained in VP resin, since iodation alkyl exists in reaction mixture, in an adsorption desorption process, as for a pyridine ring, all are mostly formed into 4 class. Therefore, it is not necessary to necessarily consider as the 4th class-ized structure beforehand.
[0017] What is necessary is to make alkyl halide react to VP resin, and just to form the pyridine ring in VP resin into 4 class, in transforming the pyridine ring in VP resin to the 4th class-ized structure of a general formula (3) beforehand and preparing an adsorbent.
[Formula 4]



(4)

(R shows an alkyl group or hydrogen among a formula, and X shows a halogen atom)
By using VP resin which has the pyridine ring of said the 4th class-ized structure, adsorption separation of the rhodium complex anion contained in it can be carried out from the reaction generation liquid containing a rhodium complex anion. The adsorption reaction in this case is as a degree type.
[Formula 5]



(5)

[0018] Said reaction is carried out in an organic solvent based on an ion exchange reaction. The reaction temperature is the temperature beyond ordinary temperature, and 200 degrees C or less of the upper limit are 180 degrees C or less preferably. Moreover, a pressure is a pressure which does not make an organic solvent boil, it is a pressure more than ordinary pressure, and the upper limit is usually below 200kg/cm2G preferably below 300kg/cm2G. The concentration of the rhodium complex anion contained in an organic solvent is rhodium metal conversion concentration, and is usually 0.3 - 10wtppm preferably 0.1 to 50 wtppm. Moreover, alcohol, a carboxylic acid, ester, the ether, a ketone, a hydrocarbon, etc. are included by the organic solvent. As alcohol, polyhydric alcohol, such as ethylene glycol besides monohydric alcohol, such as a methanol, ethanol, propyl alcohol, butyl alcohol, octyl alcohol, and benzyl alcohol, propylene glycol, and a glycerol, is mentioned. An acetic acid, a propionic acid, etc. are mentioned as a carboxylic acid. As ester, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, methyl benzoate, etc. are mentioned. Wood ether, the methylethyl ether, etc. are mentioned as the ether. A diethyl ketone, a methyl ethyl ketone, etc. are mentioned as a ketone. As a hydrocarbon, a hexane, a heptane, an octane, a cyclohexane, benzene, toluene, a xylene, etc. are mentioned. The desirable organic solvents used by this invention are a methanol and an acetic acid.
[0019] Although VP resin is adsorbed, as for the complex anion which contains the rhodium dissolved in an organic solvent by said reaction, it is desirable to use the liquid ambient atmosphere which contains a carbon monoxide for stabilization of that complex in this case, when a complex is a carbonyl complex. In this case, that carbon monoxide concentration is CO partial pressure of the gas in that liquid and vapor-liquid equilibrium, and is good to make [0.01kg/cm2 or more] it 0.07kg/cm2 or more preferably. As equipment to which VP resin and the solution containing a rhodium complex anion are contacted, the solid-liquid contactor of the conventional various kinds is used. As such equipment, the contactor of a fixed-bed method, the contactor of a suspension floor method, etc. can be mentioned.
[0020] In this invention, the rhodium complex by which the adsorbent was adsorbed contacts the oxygenated compound and/or organic solvent which contain iodation alkyl in this adsorbent, and carries out desorption of the rhodium complex. Under the present circumstances, this solvent for desorption needs to include a carbon monoxide because of rhodium carbonyl complex stabilization, and that concentration is good to make 0.01kg/cm2 or more into 0.07kg/cm2 or more preferably with CO partial pressure of the gas in that liquid and vapor-liquid equilibrium. In this invention, mixed solvents, such as an oxygenated compound which contains in this solvent for desorption the iodation alkyl obtained at the iodation alkyl recovery process, an acetic acid, methyl acetate, and water, can be used, and this solvent contacts the reaction generation gas which contains CO and iodation alkyl at this iodation alkyl recovery process, and is dissolving CO enough. Furthermore, the oxygenated compound obtained with the distillation process, an acetic acid, methyl acetate, water, etc. can be mixed and used for this solvent for desorption.
[0021] After the oxygenated compound used as a reaction raw material in this invention introducing this into an iodation alkyl recovery process, carrying out dissolution recovery of the iodation alkyl which reaction generation gas is contacted here and contained in that gas, mixing the more volatile component obtained from a distillation process by the oxygenated compound containing this iodation alkyl and using this mixture as a solvent for desorption in a desorption process, it is desirable in introducing to a carbonylation reaction process.

[0022] The carbonylation process to which the oxygenated compound and carbon monoxide in this invention are made to react is carried out using the rhodium complex compound catalyst which the above mentioned VP resin was made to support by making a methanol and a carbon monoxide react under existence of iodation alkyl and in an organic solvent. This carbonylation reaction can be carried out using various reactors. As a format of such a reactor, the fixed bed, a mixing chamber, an expansion floor, etc. are mentioned. The catalyst fill in a reactor is good to choose to 2 - 25wt% to the solution in a reactor, generally, in the case of a mixing chamber reactor, although it is 2 - 40wt%. Moreover, in a fixed bed reactor, it is good to choose to 2 - 25wt% with an expansion floor reactor 20 - 40wt%.
[0023] Although various kinds of well-known things are conventionally used as an organic solvent (reaction solvent), generally that in which a carbon number contains two or more carbonyl group content organic solvents is used. As such an organic solvent, although carboxylic acids and carboxylate, such as an acetic acid and methyl acetate, are mentioned, it is desirable to use a methanol and an acetic acid. Moreover, an organic solvent can contain water. in this case, the content of the water in an organic solvent -- the moisture concentration in reaction generation liquid -- 0.05 - 50wt% -- it is the amount which becomes 0.5 - 10wt% still more preferably 0.1 - 20wt% preferably. As iodation alkyl, although the iodation alkyl of carbon numbers 1-5 is used, use of a methyl iodide is desirable especially.
[0024] The amount of reaction solvents in a reactor is good to specify to oxygenated compound (methanol and/or wood ether) 1 weight **** more than the 0.30 weight section. The desirable amount of organic solvents is more than the 2.40 weight sections to the oxygenated compound 1 weight section. While the labile of the rhodium complex which is the active center of a catalyst by holding the amount of organic solvents in a reaction solution to said within the limits is raised, the joint stability of a rhodium complex and VP resin can also improve, it is a high rate of reaction, and the desorption of the rhodium from VP resin can be prevented effectively, and the carbonylation reaction of an oxygenated compound can be advanced smoothly. In a still more important thing, by holding the amount of organic solvents in a reactor in the aforementioned range, a rhodium complex can exist in stability under very low CO partial pressure condition of 7kg/cm2, and the carbonylation reaction of an oxygenated compound can be advanced with a high rate of reaction. It becomes unnecessary for this to use a proof-pressure container special as a reactor, it can save reactor cost sharply, and means that a practical economical acetic-acid process is acquired.
[0025] CO partial pressure at the time of performing the carbonylation reaction of an oxygenated compound (carbon monoxide partial pressure) is 10kg/cm2 or more preferably that what is necessary is just 7kg/cm2 or more. Even if it makes CO partial pressure high especially, a reaction rate seldom improves, the advantage on the reaction according to rank is not acquired, but the upper limit of the CO partial pressure is good from an economical viewpoint to make it about 30kg/cm2. Therefore, CO partial pressure is preferably good to specify [7-30kg/cm2] in the range of 10-20kg/cm2. By holding CO partial pressure in such range, it becomes possible especially about total reaction pressure 15-40kg/cm2G and to hold [economical 15-60kg/cm2G and] to the low voltage still more preferably below 15-30kg/cm2G.
[0026] Although 140-250 degrees C of reaction temperature in a carbonylation reaction are 160-230 degrees C preferably, the upper limit is suitably selected according to the thermal resistance of VP resin to be used. Moreover, the abundance of the iodation alkyl in the system of reaction is 5 - 30 % of the weight preferably one to 40% of the weight among the solution in a reactor. furthermore, the rhodium concentration in the system of reaction -- the inside of the solution in a reactor -- 50 or more wtppms are 400 or more wtppms more preferably 300 or more wtppms. In addition, the rhodium concentration said here is wt% to the solution except VP resin out of a reactor of the amount of rhodium metals.
[0027] According to the format of a reactor, a convention of the amount of the organic solvent in a reactor is performed as follows. In a batch type reactor, it considers as the amount of the organic solvent to the oxygenated compound in the raw material liquid taught to the reactor. Since oxygenated compound concentration decreases with advance of a reaction, the concentration of the organic solvent in a reactor becomes more than a preparation raw material. It is equal to the presentation of the reaction generation liquid which the solution in a reactor is mixed by homogeneity at a mixing chamber

circulation type reactor, and is extracted from a reactor outlet on parenchyma. That is, it is the amount of the organic reaction solvent to the oxygenated compound in the resultant extracted from a reactor outlet on parenchyma as a convention of the amount of the organic solvent in a reactor in this case. In a piston flow type reactor, it is set as an amount of the organic solvent to the oxygenated compound in [all / that is supplied to a reactor] supply liquid. In this case, since oxygenated compound concentration decreases and the amount of an organic solvent increases as it goes to an outlet from a reactor inlet port, the amount of the organic solvent to an oxygenated compound increases as it goes to a reactor outlet. Therefore, it is specified as the amount of the organic solvent to the oxygenated compound in [all / that is supplied to a reactor inlet port as an amount of organic solvents] supply liquid.

[0028] In the carbonylation reaction in the case of using a methanol as an oxygenated compound, the side reaction of the following reaction formula (7) and (8) occurs with the main reaction of the following reaction formula (6).

$CH_3OH+CO \rightarrow CH_3COOH$ (6)

$CH_3COOH+CH_3OH \rightleftharpoons CH_3COOCH_3+H_2O$ (7)

$2CH_3OH \rightleftharpoons CH_3OCH_3+H_2O$ (8)

[0029] In this invention, in order to manufacture an acetic acid with sufficient yield, said side reaction (7) and (8) are stopped, and it is necessary to advance the carbonylation reaction (6) of an oxygenated compound alternatively. For that, it is effective to use the thing containing methyl acetate or water as an organic solvent. When making methyl acetate exist in the system of reaction and raising acetic-acid yield, as for methyl acetate, it is desirable to add this to an oxygenated compound beforehand and to supply the system of reaction. To the oxygenated compound 1wt section, preferably, methyl acetate is good to add at a rate more than 3wt sections, can control the byproduction of methyl acetate by this, and can raise acetic-acid yield more than 1.5wt sections. Moreover, when making addition water exist in the system of reaction and raising acetic-acid yield, as for addition water, it is desirable to add this to an oxygenated compound beforehand and to supply the system of reaction. To the oxygenated compound 1wt section, preferably, addition water is good to add at a rate more than 0.5wt section, can control the byproduction of methyl acetate by this, and can raise acetic-acid yield more than 0.3wt sections.

[0030] In this invention, even if it uses the acetic-acid solvent which contains neither methyl acetate nor water as an organic solvent, by carbonylating an oxygenated compound, an oxygenated compound invert ratio can control the byproduction of methyl acetate, and can raise acetic-acid yield 96% or more, until it becomes 99% or more preferably. In this case, the oxygenated compound concentration in reaction generation liquid is good less than [0.3wt%] and to adjust an oxygenated compound invert ratio so that it may become less than [0.2wt%] preferably.

[0031] Reactors, such as a bubbling tower mold reactor which agitates the churning mixing type reactor which agitates reaction mixture by the impeller, and reaction mixture by air bubbles as a reactor used for a carbonylation of an oxygenated compound, can be used preferably. The example of the reactor containing these reactors is shown in drawing 1 - drawing 3 . Drawing 1 is the explanatory view of the reactor which consists of a churning mixing type reactor. In this drawing, 1 is a reactor. 2 shows an impeller and 4 shows a condensator. In order to perform the carbonylation reaction of an oxygenated compound using the reactor shown in drawing 1 , after filling up a reactor 1 with a catalyst, it is first filled up with the mixed liquor which consists of an oxygenated compound, a reaction solvent (organic solvent), and iodation alkyl through Rhine 5. Subsequently, while rotating an impeller 2, the mixed liquor which consists of an oxygenated compound, a reaction solvent, and iodation alkyl is supplied in a reactor from Rhine 5, the reactant gas which contains a carbon monoxide through Rhine 6 is introduced in a reactor, and it is made to blow off in liquid through the blow-of-gas nozzle 7. Reaction mixture is extracted from a reactor through Rhine 8. Moreover, although a unconverted gas (CO) and the evaporated reaction mixture are extracted out of a reactor through Rhine 12, a condensator 4, and Rhine 13, a part of reaction mixture [at least] evaporated in this case is condensed with a condensator 4, and it is returned in a reactor.

[0032] Drawing 2 is the explanatory view of the reactor which consists of a bubbling tower mold reactor of an external circulation format. In drawing 2 , in 21, a vertical mold reaction cylinder and 22 show the

1st gas separation tub, 23 shows the 2nd gas separation tub, and 49 shows a condensator. The vertical mold reaction cylinder 21 consists of a hollow barrel. The blow-of-gas nozzle (gas port) 38 for making gas blow off in the lower part in a reaction cylinder is arranged by this reaction cylinder 21 lower part, and the gas installation tubing 28 is connected with this blow-of-gas hole. The 1st gas separation tub 22 is connected with the upper limit of the reaction cylinder 21 through the short pipe 26 of a reverse truncated-cone configuration. It consists of a sealing barrel which has the bigger cross section as the horizontal section product of the reaction cylinder 21 with this same or 1st gas separation tub 22 than it, and the gas extract tubing 30 for extracting the gas divided into that top plate 25 within that tub out of a tub is connected, and the condensator 49 is connected with this gas extract tubing 30.
[0033] The lower part in the 2nd gas separation tub 23 and the lower part in the reaction cylinder 21 are connected by piping 35. The upper limit of piping 35 connected with the lower limit of the 2nd gas separation tub 23 through the short pipe 34 of a reverse truncated-cone configuration, and the lower limit of the piping 35 is connected with the reaction cylinder bottom section. The liquid supply pipe 37 for supplying a liquid to the lower part in a reaction cylinder is connected with piping 35. It is not necessary to make this liquid supply pipe 37 not necessarily able to connect with piping 35, and it can also be made to connect with the pars basilaris ossis occipitalis or the lower part of the reaction cylinder 21.
[0034] The upper part in the reaction cylinder 21 and the inside of the 2nd gas separation tub 23 are connected for piping 31. The end of piping 31 is connected with the peripheral wall of the reaction cylinder upper part, and the other end is connected with the peripheral wall of the 2nd gas separation tub. The 2nd gas separation tub 23 consists of a sealing barrel, the gas extract tubing 32 for extracting the gas separated within the tub out of a tub is connected with the top plate 33, and the liquid extract tubing 29 for extracting the liquid in a tub out of a tub is connected with the peripheral wall. Moreover, the liquid extract gas entrainment prevention plate 36 is arranged in the 2nd gas separation tub 23. This thing may be for preventing that gas is involved in into a liquid and the extract of a liquid is performed, and it may be monotonous, or you may be a gryposis plate, and especially that configuration is not restrained. The gas extract tubing 32 can be made to connect with the upper part or the gas extract tubing 30 of the 1st gas separation tub.
[0035] the ratio of horizontal section product [of the 1st gas separation tub 22] S (2), and horizontal section product [of the reaction cylinder 21] S (1) -- S(2) / S (1) -- 1-10 -- it is the range of 2-5 preferably. moreover, the ratio of horizontal section product [of the 2nd gas separation tub 23] S (3), and horizontal section product [of the reaction cylinder 21] S (1) -- S(3) / S (1) -- 0.5-5 -- it is the range of 1-3 preferably. the ratio of bore R (1) in the reaction cylinder 21, and height H (1) -- H(1) / R (1) -- 5-100 -- it is 10-20 preferably.
[0036] In the reactor shown in drawing 2 , although the blow-of-gas nozzle 38 may be a single pipe nozzle, it can be the annular nozzle which has many blow-of-gas holes in the peripheral wall of a ring-like shell.
[0037] Various modification is possible for the reactor of the structure shown in drawing 2 , for example, piping 31 can be arranged so that the inclination may descend toward the 2nd gas separation tub 23, it can be replaced with the short pipe 26 and short pipe 27 which are connected with the upper limit and lower limit of the reaction cylinder 21, respectively, and can also use the board which has opening in the center section.
[0038] In order to perform the carbonylation reaction of an oxygenated compound using the reactor of the structure shown in drawing 2 , after being filled up with a catalyst in the reaction cylinder 21, it is first filled up with raw material mixed liquor in a reactor from the liquid supply pipe 37. Next, while supplying raw material mixed liquor in the reaction cylinder 21 from the liquid supply pipe 37, the reactant gas containing a carbon monoxide is made to blow off from the gas installation tubing 28 in a liquid through the blow-of-gas nozzle 38. The reactant gas which blew off from the nozzle 38 in the liquid serves as air bubbles, and goes up the inside of a liquid, and a catalyst goes up the inside of a reaction cylinder with a liquid according to the gas lift effectiveness in that case. By rise of such a catalyst, distribution of the catalyst to the inside of the liquid in a reaction cylinder is attained, and the

smooth carbonylation reaction of an oxygenated compound and CO is performed in a reaction cylinder.
[0039] The reaction mixture obtained by the carbonylation reaction within a reaction cylinder flows in the 1st gas separation tub 22 currently arranged above the reaction cylinder including a unconverted gas (CO) and a catalyst, and is held in this 1st gas separation tub. In drawing 2 , S shows the oil level of reaction mixture. In this 1st gas separation tub 22, stripping of the gas constituents contained in reaction mixture and the evaporated reaction mixture is carried out to up space from an oil level, and it is extracted out of a tub through the gas extract tubing 30 and a condensator 49. In this case, a part of evaporated reaction mixture [at least] is condensed with a condensator 49, and it is returned to the 1st gas separation tub 22.
[0040] With the reaction mixture in which the catalyst which went up the inside of the reaction cylinder 21 with the liquid contains a unconverted gas, the gas constituents which flowed in the 2nd gas separation tub 23 through piping 31 from the reaction cylinder upper part, and were contained in reaction mixture here are separated, and the separated gas constituents and the evaporated reaction mixture are extracted through piping 32. On the other hand, reaction mixture is extracted through the liquid extract tubing 29. Since the gas entrainment prevention plate 36 is arranged in the 2nd gas separation tub 23, mixing of the gas to the reaction mixture extracted is prevented, and reaction mixture can be extracted through the liquid extract tubing 29 in the state of standing. With the self-weight, the reaction mixture and the catalyst from which gas constituents were separated circulate in the lower part in the reaction cylinder 21 through piping 35 from the 2nd gas separation tub 23. The catalyst which circulated with reaction mixture in the lower part in the reaction cylinder 21 goes up the inside of the reaction cylinder 21 again.
[0041] As for the force to which a catalyst is moved upward, the force to which the linear velocity of a liquid moves a catalyst up with regards to an above linear velocity of a liquid, so that it is large also becomes large. Therefore, a catalyst particle can be moved up by adjusting so that it may become larger than the gravity which drops the catalyst which exists the linear velocity of a liquid in a liquid. However, since horizontal section product [of the 1st gas separation tub 22] S (2) is larger than horizontal section product [of the reaction cylinder 21] S (1) in the case of the reactor shown in drawing 2 , If the linear velocity of a liquid enters in the 1st gas separation tub, it will become small rapidly, and migration into the 1st gas separation tub of a catalyst is prevented, and flows into the 2nd gas separation tub 23 alternatively through piping 31 from the upper part in the reaction cylinder 21.
[0042] As it is the above, in the equipment shown in drawing 2 , the liquid style which goes up the inside of the reaction cylinder 21, and the circulating flow through which it circulates from the upper part of the reaction cylinder 21 to the lower part in the reaction cylinder 21 through piping 31, the 2nd gas separation tub 23, and piping 35 are formed.
[0043] Drawing 3 is the explanatory view of the reactor which consists of a bubbling tower mold reactor of an internal circulation format. In this drawing, 51 shows a reactor and this thing consists of a gas separation tub 54 connected with the reaction cylinder 52 and its upper limit. The horizontal section product of the gas separation tub 54 is larger than the horizontal section product of the reaction cylinder 52. 53 shows a container liner. In order to perform the carbonylation reaction of an oxygenated compound using this reactor, after being filled up with a catalyst in a reactor, it is first filled up with raw material mixed liquor from Rhine 56. Next, while supplying raw material mixed liquor into a reactor from Rhine 56, the reactant gas containing a carbon monoxide is made to blow off from Rhine 57 in the state of air bubbles into liquid through the blow-of-gas nozzle 58 of the pars basilaris ossis occipitalis of a container liner 53. Of jet into the liquid of this mixed gas, in a container liner 53, the upward flow which consists of mixture of a liquid and the air bubbles of mixed gas is formed, and with formation of this upward flow, downward flow arises in the annular gap section between a container liner 53 and the reaction cylinder 52, and circulating flow is formed in a reactor. It goes together in the style of [the] a rise liquid, and the catalyst distributed in a liquid goes up the inside of a container liner 53. And these oxygenated compounds, a carbon monoxide, and a catalyst contact mutually between the rise, and the carbonylation reaction of an oxygenated compound is attained.
[0044] The vapor-liquid mixture which goes up a container liner 53 flows in the gas separation tub 54

connected with the upper limit of the reaction cylinder 52, and separation of gas constituents, such as a unconverted gas (CO), is performed from reaction mixture. On the other hand, a catalyst descends the annular gap circles between a container liner 53 and the reaction cylinder 52, after the liquid has distributed, and it circulates at the pars basilaris ossis occipitalis of the reaction cylinder 52. Although the gas constituents separated in the gas separation tub 54 are discharged through Rhine 60, a condensator 55, and Rhine 61 with the evaporated reaction mixture, a part of reaction mixture [at least] evaporated in this case is condensed with a condensator 55, and it is returned in a reactor. Reaction mixture is extracted from a reactor through Rhine 59.

[0045] Next, one example of the flow sheet of the approach of this invention is shown in drawing 4 . drawing 4 -- setting -- 1 -- a carbonylation reactor, and 2 and 3 -- an adsorbent packed column and 4 -- an evaporation tub and 5 -- a distilling column and 6 -- a vapor-liquid-separation machine, and 7 and 8 -- a scrubber and 9 -- a heat exchanger and 10 -- a condensator -- each ****. The carbonyl reactor 1 can be the thing of various kinds of above mentioned methods, and the interior is filled up with the rhodium complex compound catalyst supported to VP resin. It fills up with the adsorbent with which the adsorbent packed columns 2 and 3 show adsorbent to a rhodium complex in the interior. In order that scrubbers 7 and 8 may raise vapor-liquid contacting efficiency to the interior, it fills up with the filler. Various kinds of well-known things, for example, a raschig ring, Tellerette, Paul ring, a saddle, Lessing ring, etc. can be mentioned conventionally.

[0046] According to the flow sheet shown in drawing 4 , the acetic-acid manufacture approach of this invention is explained in full detail below. The oxygenated compound containing the iodation alkyl and the rhodium complex which the oxygenated compound was supplied through Rhine 21 and 26, and were extracted through Rhine 41 from the adsorbent packed column 2 is supplied to a reactor 1 through Rhine 44 and 53. Furthermore, a carbon monoxide is supplied to this reactor 1 through Rhine 22. In a reactor 1, the carbonylation reaction of an oxygenated compound and a carbon monoxide is performed under existence of the rhodium complex supported by VP resin. In the case of the flow sheet shown in this drawing 4 , as a reaction solvent, the oxygenated compound is made to serve a double purpose. When using a reaction solvent different from an oxygenated compound, it can mix to the oxygenated compound passing through Rhine 21 or Rhine 26, and the reaction solvent can also be supplied to direct reaction equipment 1 apart from an oxygenated compound.

[0047] From a reactor 1, reaction generation liquid is extracted through Rhine 31, and reaction generation gas is extracted through Rhine 61. Reaction generation liquid consists of an acetic acid, methyl acetate, wood ether, a propionic acid, iodation alkyl, hydrogen iodide, a rhodium complex, a methanol, etc., and the content of the rhodium complex is metal rhodium conversion, and is usually 0.3 - 10wtppm 0.1 to 50 wtppm. Reaction generation gas consists of iodation alkyl, hydrogen iodide, hydrogen, methane, and CO2 grade. Reaction generation liquid passes along a heat exchanger 9, and is introduced into the adsorbent packed column 3 through Rhine 33, Rhine 39, a bulb 12, and Rhine 40. On the other hand, reaction generation gas is introduced into a scrubber 7, and contacts the oxygenated compound introduced into the scrubber 7 through Rhine 28 here. Thereby, the iodation alkyl in reaction generation gas dissolves into an oxygenated compound, and separation recovery is carried out from reaction generation gas. Moreover, separation recovery of the hydrogen iodide contained in reaction generation gas, methyl acetate, wood ether, etc. is carried out into an oxygenated compound. The oxygenated compound containing this iodation alkyl is extracted from a scrubber 7 through Rhine 62, and is introduced into the adsorbent packed column 2 through Rhine 64, a heat exchanger 9, Rhine 32, Rhine 35, a bulb 13, and Rhine 36.

[0048] In said heat exchanger 9, indirect heat exchange between reaction generation liquid and the oxygenated compound containing iodation alkyl is performed, the temperature of reaction generation liquid can be lowered by this, and the temperature of the oxygenated compound containing iodation alkyl is raised. Although the temperature of reaction generation liquid before going into a heat exchanger 9 is 160-200 degrees C, it usually turns into temperature (usually 100-140 degrees C) which was able to be lowered about 40-80 degrees C after said heat exchanger passage. Although the temperature of the oxygenated compound which, on the other hand, contains the iodation alkyl before